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Kinetics and Isotope Effect of Ammonia Synthesis over Ruthenium

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Kinetics and isotope effect of ammonia synthesis over a ruthenium catalyst were investigated at 346–410°C under reduced pressures. A rate equation $R = kP_{N_2}P_{H_2}{}^0P_{NH_3}{}^0$ was obtained. Deuterium isotope effect was hardly detected. It is concluded from these that the rate of synthesis is controlled by dissociative adsorption of nitrogen. The lack of isotope effect over Ru is successfully interpreted from the view previously proposed for the synthesis over Fe and applied to Mo. Relevant works are also discussed.

INTRODUCTION

It is generally accepted that the rate-determining step in ammonia synthesis lies in dissociation of nitrogen molecule. An unusual inverse isotope effect observed in this synthesis over iron (*1*, *2*) or molybdenum (*3*) catalyst has been successfully interpreted on the accepted mechanism as represented by

$$N_2 \xrightarrow{\wedge} 2N \text{ (or } 2NH) \overset{H_2}{\rightleftharpoons} NH_3, \qquad (1)$$

$$N_2 \xrightarrow{\wedge} 2N \text{ (or } 2ND) \overset{D_2}{\rightleftharpoons} ND_3, \qquad (1')$$

where the rate-determining dissociation of nitrogen is retarded by the previously adsorbed and dissociated species (N or NH), the amount of which is decided by the equilibrium

$$N(a) + \tfrac{3}{2}H_2 = NH_3, \qquad (2)$$

or

$$NH(a) + H_2 = NH_3. \qquad (2')$$

The inverse isotope effect in the observed rate of synthesis is quite reasonable as the effect on the amount of retarding species on the surface, because the equilibrium of the Eqs. (2) or (2′) is favorable for deuterium and thus the deuterium system should give a lower concentration of the retarding species on the surface.

If this view on the inverse isotope effect is true, it should be expected that, when there is no retarding species on the surface, little or no isotope effect is realized in ammonia synthesis, although such a case has not been reported yet. This prediction has been tested over ruthenium which is expected to have less affinity to adsorbed nitrogen than iron or molybdenum.

EXPERIMENTAL METHODS

The apparatus employed was a closed circulating system with liquid nitrogen traps and the experimental procedures were similar to those described in the previous papers (*1*–*3*). The catalyst was a ruthenium catalyst supported on celite which was pretreated with hot dilute hydrochloric acid for 48 hr. The catalyst was prepared by impregnation with aqueous solution of ruthenium trichloride followed by heating at 500°C for 3 hr. It was treated by dry hydrogen at 350°C for 48 hr. The sample contained 5.0 wt % ruthenium. The total weight of the catalyst was 1.50 g.

RESULTS

Synthesis runs were made over the ruthenium catalyst at 346°C under three different total pressures 150, 300, and 600 mm Hg. The synthesis rates were so slow that it took 10–20 hr to obtain one datum. The results of this series (A) are shown in Fig. 1 as a plot of observed rate of am-

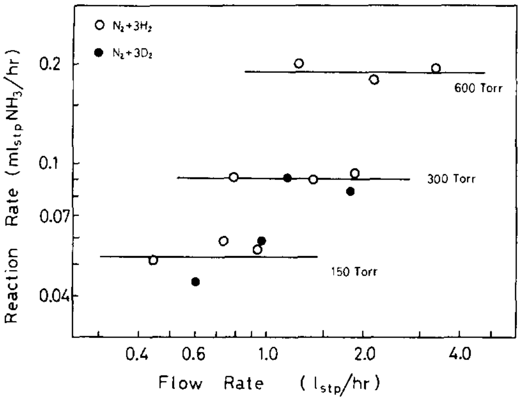

FIG. 1. Isotope effect and flow rate dependence of reaction rate at 346°C (Ser. A): ○, hydrogen system ($N_2 + 3H_2$); and ●, deuterium system ($N_2 + 3D_2$).

monia synthesis against flow rate. The change of reactant gas was performed by short (ca. 1 min) evacuation. As shown in Fig. 1, the rate of synthesis does not depend upon the flow rate, and the deuterium isotope effect is hardly detected.

After this series of runs, when the catalyst was evacuated at 346°C for 3 hr, there was a sudden decrease in activity, which seemed to be due to sintering of the catalyst occurred with heating *in vacuo*.* Therefore, no more long evacuation was made so that the activity of catalyst remained at a steady value. Those runs made with the catalyst after this accident is designated as B series.

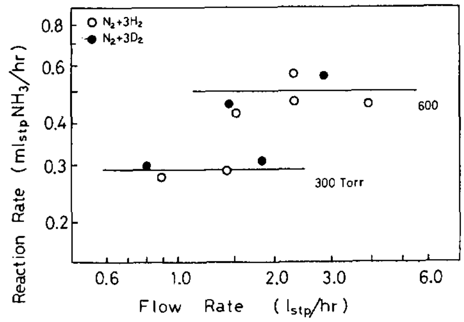

FIG. 2. Isotope effect and flow rate dependence of reaction rate at 410°C (Ser. B): ○, hydrogen system; and ●, deuterium system.

The synthesis runs of B series were made at 346–410°C under 300–600 mm Hg. The results at 410°C are shown in Fig. 2. It was again found that the synthesis rate does not depend on the flow rate, and that there is no deuterium isotope effect. The effect of temperature is shown in Fig. 3 as an Arrhenius plot of the synthesis rate which was obtained as the mean value of the observed rates at one temperature. An activation energy value of 24.0 kcal/mole is obtained from this plot.

The pressure dependency of the synthesis rate is shown in Fig. 4 with both series A and B. The slope of the straight line gives an order of 0.95, i.e., the synthesis rate is approximately proportional to total pressure.

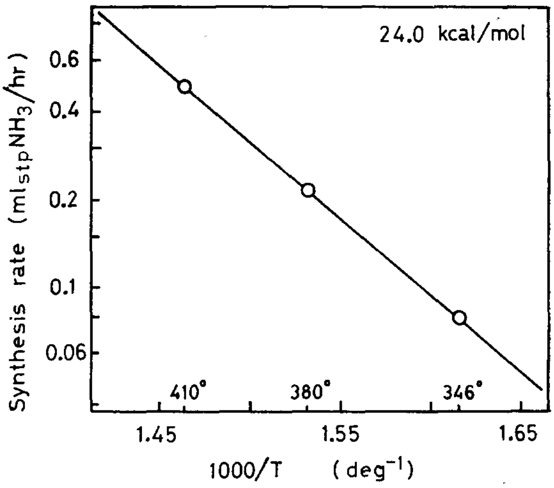

FIG. 3. Arrhenius plot of the reaction rate at the pressure of 600 mm Hg (Ser. B); each point is an average value of several data.

Another series of runs (Ser. B) were made changing hydrogen pressure from 113 to 450 mm Hg with a fixed nitrogen pressure of 37.5 mm Hg. The results are shown also in Fig. 4. It is clear that the synthesis rate does not depend on hydrogen pressure. Since it is independent of the flow rate, the synthesis rate is independent of ammonia pressure. After all the rate of synthesis R is described as follows

$$R = kP_{N_2}P_{H_2}{}^{0}P_{NH_3}{}^{0}, \qquad (5)$$

with $k_H = k_D$.

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* It was shown over nickel film that the sintering is prevented by the presence of reactant gas (*4*).

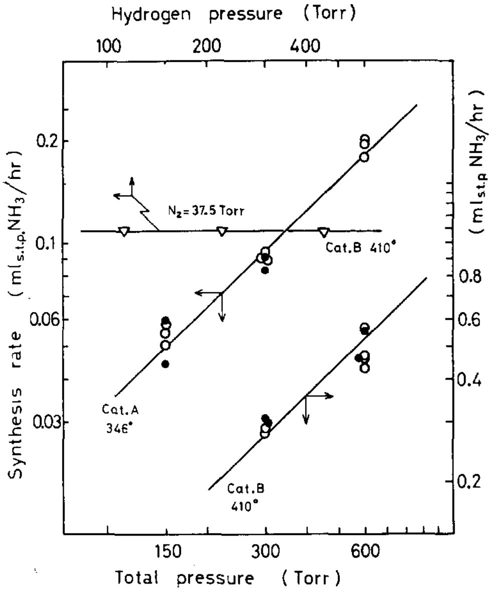

FIG. 4. Dependence of reaction rate on total pressure (○); and hydrogen pressure (△) over ruthenium catalyst; ●, deuterium system.

DISCUSSION

It was previously shown that the rate of ammonia synthesis over iron and molybdenum can be described by an equation

$$R = \frac{kP_{N_2}}{(1 + KP_{NH_3}/P_{H_2}^{1.5})^2}, \tag{6}$$

where K is the equilibrium constant of the reaction

$$NH_3 = N(a) + 1.5H_2, \tag{7}$$

and represents the relative strength of adsorption bond of nitrogen atom. The rate Eq. (5) obtained for Ru in this study is devoid of the denominator of Eq. (6). However Eq. (5) may be considered as a special case of Eq. (6), where the term $KP_{NH_3}/P_{H_2}^{1.5}$ is neglected against unity. This should be the case when KP_{NH_3} is small enough. Indeed, the partial pressure of ammonia in the catalyst bed of Ru was extremely low because of the low activity of the catalyst. It was less than 0.1 mm Hg at most.

The relative magnitude of K on Ru may be estimated by the general rule in chemisorption as formulated by Tanaka and Tamaru (*5*). They were successful in correlating the exponent (δ) of Temkin equation for decomposition of ammonia

$$R = k\left(\frac{P_{NH_3}^{2}}{P_{H_2}^{3}}\right)^{\delta}, \tag{8}$$

to the heat of formation of metal oxide of the highest oxidation state $-\Delta H_0{}^0$ (*6*). Since, as accepted, Eq. (8) may be obtained by approximation from an equation of the type

$$R = \frac{k'(KP_{NH_3}/P_{H_2}^{1.5})^2}{(1 + KP_{NH_3}/P_{H_2}^{1.5})^2}, \tag{9}$$

δ is closely related to K, and varies from zero to unity when K varies from infinity to zero. Since, as shown by Tanaka and Tamaru (*6*), the value of δ observed over various metals decreases with increase in $-\Delta H_0{}^0$, K should be smaller on Ru than on Fe or Mo.

In order to examine this prediction, those values of K are quoted from the previous reports together with the values of activation energy and tabulated in Table 1.

TABLE 1
RATE CONSTANTS OF Eq. (6) AND $-\Delta H_0{}^0$ FOR METALS

	Molybdenum[a]	Iron	Ruthenium
$-\Delta H_0{}^0$ (kcal/Me-atom)	180.4	97.6	52.5
K (atm$^{0.5}$)	1900	650[b]	Neg.
Temp. (°C)	(330)	(305)	(345–410)
Activation energy of k (kcal/mole)	14	20[c]	24

[a] Ref. (*3*).
[b] Unpromoted iron (*2*).
[c] Doubly promoted iron (*1*).

It is shown that the kinetic parameters over metals are correlated with $-\Delta H_0{}^0$ as expected. Accordingly it may be reasonable to assign a small value to K over Ru. The rate equation obtained over Ru may be considered as a special case of Eq. (6) where the term $KP_{NH_3}/P_{H_2}^{1.5}$ is neglected.

All the information obtained in this study suggest that the rate of ammonia synthesis over Ru is determined by the step of dissociation of nitrogen. The observed absence of isotope effect is clearly due to the absence of retardation by ammonia which is caused by the weak adsorption of dissociated nitrogen. This result reconfirms the previous interpretation of the inverse isotope effect in ammonia synthesis as described in the "Introduction." There have been proposed some other interpretations for the inverse isotope effect.

Logan and Philp (*7*) have reanalyzed the previous data (*1*) on the doubly promoted iron catalyst by means of electronic computer and separated the deuterium isotope effect into two parts, one is the inverse isotope effect resulted from the thermodynamic difference in concentration of adsorbed nitrogen atom instead of imino radical originally proposed by Ozaki *et al.* (*1*), and another is a normal isotope effect which seems to be ascribed to the "hydrogen-promoted" dissociative adsorption of nitrogen.

Since it has been known that both the isotopic exchange in nitrogen (*8, 9*) and the adsorption of nitrogen (*10*) are promoted by coexisting hydrogen on the doubly promoted iron, some extent of kinetic deuterium isotope effect may be expected for the dissociative adsorption of nitrogen. However the ratio k_H/k_D estimated by Logan and Philp (*7*) is as large as 2.0 at 302°C. If this value is true, this should be found in Tamaru's experiment, where he failed to find the deuterium isotope effect in the adsorption of nitrogen, whereas there was an excuse for Logan and Philp that the adsorbed nitrogen measured by Tamaru might be undissociated. The existence of undissociated nitrogen was demonstrated over unpromoted iron (*11*).

In this respect, the present case of ammonia synthesis over Ru is suitable for the examination of the kinetic isotope effect in the adsorption of nitrogen because there is no trouble with retardation by ammonia. The present data are not accurate enough to determine small difference in the rates, but still feasible to detect a ratio k_H/k_D of 2.0. The deuterium isotope effect in the adsorption of nitrogen, if any, is estimated to be 1.1 of k_H/k_D at highest as judged from the errors involved, and can not be as high as 2.0. It seems that the ratio k_H/k_D for the adsorption of nitrogen is near to unity on the doubly promoted iron, too.*

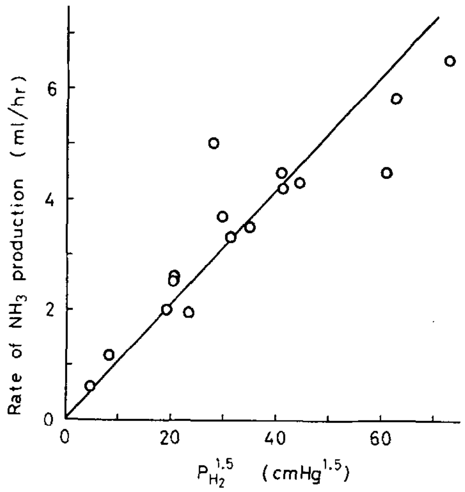

FIG. 5. Replot of hydrogen pressure dependence of the rate of reaction between hydrogen and adsorbed nitrogen over doubly promoted iron catalyst at 250°C from Tamaru's paper (*12*). Amount of chemisorbed nitrogen is 33–37 ml (stp).

Another completely different intrepretation of the inverse isotope effect was raised by Tamaru (*12*) who found that ND_3 is produced 4–5 times faster than NH_3 from previously adsorbed nitrogen. It was concluded on the basis of this result that the isotope effect in the overall reaction is attributed to the effect in the reaction between chemisorbed nitrogen and hydrogen, that is, an interpretation from kinetic ground.

However it is well known and generally accepted that light hydrogen usually reacts faster than heavy one in the case of kinetic primary isotope effect. The inverse isotope effect as observed in the ammonia synthesis over the doubly promoted iron is unlikely as a kinetic isotope effect for the overall reaction, whereas a value, k_D/k_H of 1.7 was found in the hydrogenation of ethylene by palladium hydride at −78°C (*13*).

Two possible interpretations for Tamaru's result may be mentioned. One is that the process observed by Tamaru might be

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* This has been confirmed by the isotopic mixing in nitrogen in the presence of hydrogen which will be published very soon.

the hydrogenation of adsorbed but undissociated nitrogen, with the rate being determined by the dissociation process of the adsorbed nitrogen that is

$$N_2(a) \xrightarrow{\;\wedge\;} 2N(a) \overset{3H_2}{\rightleftarrows} 2NH_3. \qquad (10)$$

Another interpretation arises from the view reconfirmed in this study. If the rate determining step of the overall reaction is the dissociative adsorption of nitrogen, the adsorbed nitrogen atom should be equilibrated with gaseous hydrogen and ammonia by the reaction

$$N(a) + \tfrac{3}{2}H_2 = NH_3. \qquad (11)$$

Hence the effluent gas from the catalyst bed should contain different concentrations of NH_3 and ND_3 determined by the equilibrium. If this was the case with Tamaru's paper, the reaction rate which was represented by the amount of NH_3 formed in unit time should be proportional to $P_{H_2}{}^{1.5}$ instead of $P_{H_2}{}^{1.0}$ which was originally plotted in his paper. The relevant data are quoted and replotted against $P_{H_2}{}^{1.5}$ in Fig. 5. It seems that the $P_{H_2}{}^{1.5}$ plot gives a rather better fit.* Furthermore, the rate ratio R_D/R_H of 4.5 is close to the theoretical value of 5.3 (250°C) which is obtained from the equilibrium constants of the reaction (*12*).

In this manner the inverse isotope effect in the hydrogenation of adsorbed nitrogen on iron catalyst can be explained on the same ground as in the overall reaction. Thus the latter interpretation seems more probable. In conclusion, the inverse isotope effect in ammonia synthesis is convincingly thermodynamic in nature.

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* This is the same kinetics as was reported for the hydrogenation of adsorbed nitrogen on Mo (*14*).